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# Turning a yield-stress calcite suspension into a shear-thickening one by tuning inter-particle friction

James A. Richards · Rory E. O'Neill · Wilson C. K. Poon

July 13, 2020

**Abstract** We show that a suspension of non-Brownian calcite particles in glycerol-water mixtures can be tuned continuously from being a yield-stress suspension to a shear-thickening suspension—without a measurable yield stress—by the addition of various surfactants. We interpret our results within a recent theoretical framework that models the rheological effects of stress-dependent constraints on inter-particle motion. Bare calcite particle suspensions are found to have finite yield stresses. In these suspensions, frictional contacts that constrain inter-particle sliding form at an infinitesimal applied stress and remain thereafter, while adhesive bonds that constrain inter-particle rotation are broken as the applied stress increases. Adding surfactants reduces the yield stress of such suspensions. We show that, contrary to the case of surfactant added to colloidal suspensions, this effect in non-Brownian suspensions is attributable to the emergence of a finite onset stress for the formation of frictional contacts. Our data suggest that the magnitude of this onset stress is set by the strength of surfactant adsorption to the particle surfaces, which therefore constitutes a new design principle for using surfactants to tune the rheology of formulations consisting of suspensions of adhesive non-Brownian particulates.

**Keywords** Suspension · Yield stress · Shear thickening · Rheology · Calcite · Dispersants

## Introduction

A transformation has recently occurred in our understanding of the rheology of suspensions of hard non-Brownian (nB)

particles (size  $\gtrsim 2\ \mu\text{m}$ ) with repulsive interactions. Such suspensions shear thicken: their viscosity increases with applied shear rate (Barnes, 1989). It is now accepted that the stress-driven contact formation plays the dominant role (Lin et al., 2015; Clavaud et al., 2017; Comtet et al., 2017). Particles in mechanical contact cannot freely slide past one another due to Coulomb friction (Seto et al., 2013) or other mechanisms (Hsu et al., 2018; James et al., 2018). This happens when the stabilising repulsive force between particles fails to keep them separated when the applied stress increases beyond a critical threshold,  $\sigma^*$ , the “onset stress”. The close approach of particle surfaces switches on anti-sliding mechanisms (Wilson and Davis, 2000; Wyart and Cates, 2014). The additional particle motion needed on the local level to accommodate any given macroscopic strain leads to extra dissipation, so that the viscosity rises (Lerner et al., 2012).

Most industrial nB suspensions are not purely repulsive. Typically, at high enough volume fraction,  $\phi$ , there exists a yield stress,  $\sigma_y$ , below which there is no flow. Above  $\sigma_y$  the suspension shear thins and the viscosity decreases to a limiting plateau value. Practical examples span diverse sectors, from suspensions of mineral powders (Zhou et al., 1995) and polymeric latices (Heymann et al., 2002) to coal slurries (Wildemuth and Williams, 1985) and molten chocolate (Blanco et al., 2019), for which glass spheres with hydrophobic coating in water (Brown et al., 2010) may function as a generic model system. In such applications, it is important to be able to ‘tune’ the yield stress, for example in unset concrete. To allow pumping and filling of formwork,  $\sigma_y$  must not be too high (Roussel, 2007); in contrast during 3D printing of concrete, too low a  $\sigma_y$  and the unset concrete will not hold the desired shape before setting (Mechtcherine et al., 2020). It is therefore important to understand the origin of the yield stress in nB suspensions.

A finite suspension yield stress is typically traced back to residual van der Waals attraction between particles that are

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insufficiently stabilised (Bonn et al., 2017). Such particles can ‘bond’ so that above some critical  $\phi \ll \phi_{\text{rcp}}$  they form a stress-bearing network. To flow, a finite stress  $\sigma > \sigma_y$  must be applied to break the bonds and fluidise the suspension. A classic way to tune  $\phi_y$  is by adding surfactants, variously known as dispersants, plasticisers or other sector-specific terms. These adsorb onto particle surfaces, increase the minimum separation, and so reducing attraction and  $\sigma_y$ .

This explanation undoubtedly applies to colloids, where Brownian motion drives aggregation, and has been used to explain yield stress in nB suspensions (Brown et al., 2010). To see that something may be amiss in the latter case, consider an aqueous suspension of calcite particles, as found in toothpastes, paints and paper coatings. Later, we show that a  $\phi \approx 0.5$  suspension of this kind with particle dimension  $d \approx 4 \mu\text{m}$  has  $\sigma_y \approx 10^2 \text{ Pa}$  under steady shear. Dimensional analysis of the colloidal picture suggests that  $\sigma_y \sim U/d^3$ , with the energy scale  $U$  set by the van der Waals interaction. Taking  $U \sim Ad/12h$  for two spheres at surface separation  $h$  with the Hamaker constant,  $A$ , of calcite in water (Bergström, 1997), we find  $h \sim 0.01 \text{ Å}$ , far below the atomic scale. It is evident we are missing some vital physics.

The missing physics is particle contact, which, if attractive forces are present, can prevent rolling below a critical torque when the contacts are pinned (Heim et al., 1999; Estrada et al., 2011). Such adhesive contacts constrain inter-particle rolling, just as frictional contacts prevent sliding. The effect of sliding and rolling constraints acting independent or together on viscosity has been explored in a ‘constraint rheology’ framework (Guy et al., 2018), in which there are two critical stress scales, the onset stress for making frictional contact,  $\sigma^*$ , and the strength of an adhesive contact,  $\sigma_a$ .

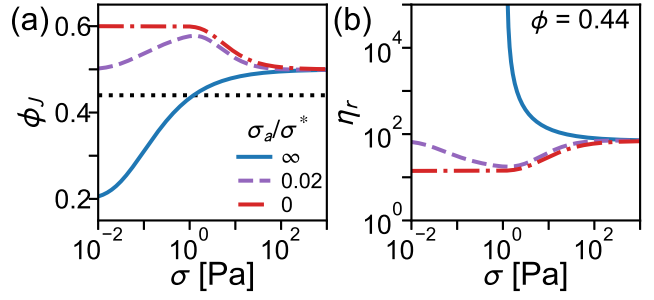
Below we review constraint rheology (Guy et al., 2018), and then consider our data for a model calcite suspension in the context of constraint rheology. The finite yield stress in the bare-particle system can be ‘tuned away’ by adding surfactants. Making sense of our observations using the constraint rheology framework allows us to interpret the role of different surfactants in such adhesive nB suspensions, which turns out to differ radically from how they act in Brownian suspensions.

## Constraint rheology of suspensions

For suspensions of hard particles, the relative viscosity,  $\eta_r$ , is controlled by the proximity to the jamming volume fraction. The viscosity divergence at some jamming point,  $\phi_J$ , is captured by the form of Krieger and Dougherty (1959),

$$\eta_r = \eta/\eta_s = [1 - \phi/\phi_J]^{-\ell}, \quad (1)$$

with  $\ell \gtrsim 2$  (Guy et al., 2015). At  $\phi \geq \phi_J$ , the system shear jams and fractures under deformation (Brown and Jaeger,



**Fig. 1** Changing the ratio of the frictional onset stress to adhesive strength,  $\theta = \sigma_a/\sigma^*$ . (a) Stress-dependent jamming point,  $\phi_J(\sigma)$ , with decreasing  $\theta$ , Eqs. 2-5. Lines: solid (blue), yield-stress ( $\sigma_a = 0.1 \text{ Pa}$ ,  $\sigma^* = 0 \text{ Pa}$ ); dashed (purple), thinning then thickening ( $\sigma_a = 0.1 \text{ Pa}$ ,  $\sigma^* = 5 \text{ Pa}$ ); dot-dashed (red), shear-thickening ( $\sigma_a = 0 \text{ Pa}$ ,  $\sigma^* = 5 \text{ Pa}$ ); and, dotted (black), example volume fraction,  $\phi = 0.44$ . Other parameters:  $\phi_{\text{rcp}} = 0.6$ ,  $\phi_\mu = 0.50$ ,  $\phi_{\text{alp}} = 0.2$ ,  $\beta = 1$ ,  $\kappa = 0.6$ . (b) Resultant flow curves at  $\phi = 0.44$  using Eq. 1 ( $\ell = 2$ ),  $\sigma_a/\sigma^*$  as in (a)

2014; Dhar et al., 2020). In the Wyart and Cates (2014) (WC) model for shear thickening,  $\phi_J$  depends on the stress-dependent fraction of frictional contacts,

$$f(\sigma) = \exp[-(\sigma^*/\sigma)^\beta], \quad (2)$$

which increases at the onset stress,  $\sigma^*$ , from  $f(\sigma \ll \sigma^*) = 0$  to  $f(\sigma \gg \sigma^*) = 1$ , with a rapidity set by  $\beta$ . The increasing fraction of frictional contacts lowers the jamming point via

$$\phi_J = \phi_\mu f + \phi_{\text{rcp}}(1 - f), \quad (3)$$

from random close packing,  $\phi_J(f=0) = \phi_{\text{rcp}}$  at  $\sigma \ll \sigma^*$ , to a lower frictional jamming point,  $\phi_J(f=1) = \phi_\mu$ , at  $\sigma \gg \sigma^*$ , whose value depends on inter-particle friction (Silbert, 2010). For a suspension at a fixed  $\phi < \phi_\mu$ , a  $\phi_J(\sigma)$  decreasing with stress gives a viscosity that increases from a low-shear plateau,  $\eta_r^0$ , to a high-shear plateau,  $\eta_r^\infty$ , Eq. 1, as observed.

Importantly, adhesive constraints that limit inter-particle rolling can also lower  $\phi_J$  (Guy et al., 2018; Richards et al., 2020). These are broken above a critical torque,  $M_a$ , set by the attractive force between particles and a surface length scale that pins the contact (Heim et al., 1999). The fraction of adhesive contacts,  $a$ , decreases rapidly above a characteristic stress,  $\sigma_a \sim M_a/d^3$ , which we model by

$$a(\sigma) = 1 - \exp[-(\sigma_a/\sigma)^\kappa], \quad (4)$$

where  $\kappa$  controls how rapidly  $a$  decreases from  $a(\sigma \ll \sigma_a) = 1$  to  $a(\sigma \gg \sigma_a) = 0$ .

With adhesive constraints alone, jamming occurs at ‘adhesive close packing’,  $\phi_J(a=1, f=0) = \phi_{\text{acp}}$ . Since the number of constraints (two rolling degrees of freedom) is the same as that in a purely frictional system (two sliding degrees of freedom), we take  $\phi_{\text{acp}} = \phi_\mu$ . If both constraints operate, jamming occurs at a lower concentration, ‘adhesive loose packing’,  $\phi_J(a=1, f=1) = \phi_{\text{alp}} < \phi_{\text{acp}}$ . This critical

Frac. frictional contacts, $f$	Frac. adhesive contacts, $a$	$\phi_J$
0	0	$\phi_{\text{rcp}}$
1	0	$\phi_\mu$
0	1	$\phi_{\text{acp}} = \phi_\mu$
1	1	$\phi_{\text{alp}}$

**Table 1** Table of jamming volume fractions in decreasing order. For quasi-monodisperse hard spheres,  $\phi_{\text{rcp}} \approx 0.64$  and  $\phi_\mu \approx 0.55$  are well documented; one simulation suggests  $\phi_{\text{alp}} \approx 0.14$

volume fraction, which is possibly related to rigidity percolation (Richards et al., 2020), is not yet precisely known; one simulation returns  $\phi_{\text{alp}} \approx 0.14$  (Liu et al., 2017). The various jamming points are summarised in Table 1.

In any actual suspension,  $0 \leq f(\sigma/\sigma^*)$ ,  $a(\sigma/\sigma^*) \leq 1$ , and  $\phi_J(\sigma)$  depends on the degree to which frictional/adhesive contacts are formed/broken by the applied stress. We use a phenomenological *ansatz* to extend Eq. 3:

$$\phi_J = f [\phi_{\text{alp}} a + \phi_\mu (1 - a)] + (1 - f) [\phi_{\text{acp}} a + \phi_{\text{rcp}} (1 - a)]. \quad (5)$$

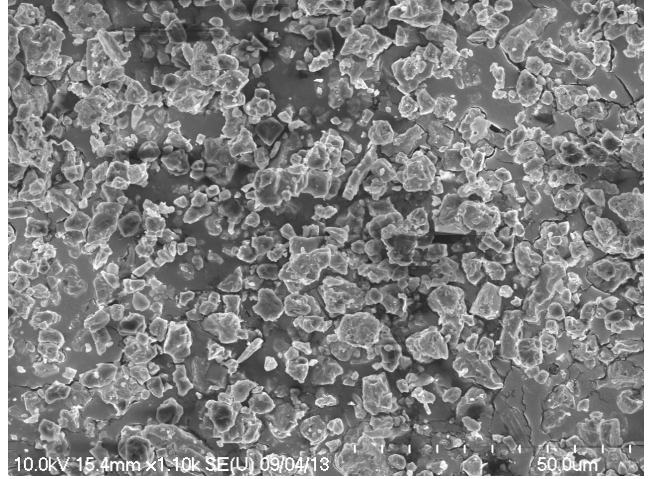
The rheology clearly depends on the ratio  $\theta = \sigma_a/\sigma^*$ . In a ‘frictional suspension’,  $\theta \gg 1$  ( $\sigma^* \ll \sigma_a$ ),  $f = 1$  at all accessible stresses and the flow is always frictional. Adhesion stabilises frictional contact networks, so that the system can jam and a yield stress develops at some rather low  $\phi_{\text{alp}}$ . Increasing the stress on a jammed system releases proportionately more adhesive constraints, so that  $\phi_J$  monotonically increases from  $\phi_{\text{alp}}$  to  $\phi_\mu$ . This monotonic  $\phi_J(\sigma)$  produces a corresponding monotonic shear-thinning  $\eta_r(\sigma)$ , Eq. 1 and Fig. 1 [solid (blue)].

In a ‘lubricated suspension’,  $\theta \ll 1$  ( $\sigma^* \gg \sigma_a$ ), increasing  $\sigma$  beyond  $\sigma_a$  rapidly releases rolling constraints while  $f \approx 0$ . Thus,  $\phi_J$  increases from  $\phi_{\text{acp}}$  (which we take to be  $= \phi_\mu$ ) towards  $\phi_{\text{rcp}}$ , until  $\sigma \rightarrow \sigma^*$  and frictional contacts start to form, whereupon  $\phi_J$  decreases towards  $\phi_\mu$ . Such a non-monotonic  $\phi_J(\sigma)$  gives rise to a corresponding non-monotonic  $\eta_r(\sigma)$ , Eq. 1 and Fig. 1 [dashed (purple)]. In this case, with no frictional contact network for adhesion to stabilise, the system cannot jam (and  $\sigma_y = 0$ ) below  $\phi_{\text{acp}}$  ( $= \phi_\mu$  for us) (Richards et al., 2020).

Within this framework, then, we may ‘tune’ a suspension in the range  $\phi_{\text{alp}} < \phi < \phi_{\text{acp}} = \phi_\mu$  from having a finite  $\sigma_y$  to having essentially  $\sigma_y \rightarrow 0$ —a many orders of magnitude change—by engineering a transition from the  $\theta \gg 1$  (frictional) regime to  $\theta \ll 1$  (lubricated) regime. Below we show how to do this using surfactants in a calcite suspension.

## Materials and methods

We studied ground calcium carbonate with a rhombohedral form [Eskal 500, KSL Staubtechnik GmbH (2007), 99%



**Fig. 2** Scanning electron micrograph of ground calcite, scale bar 50  $\mu\text{m}$

purity, density  $\rho_p = 2.7 \text{ g/cm}^3$ ,  $d_{50} = 4 \mu\text{m}$ ], Fig. 2. Ground calcite is widely used as a filler in aqueous coatings to improve abrasion resistance and finish, or as a cheap extender. Powder was dispersed in glycerol-water mixtures using vortex and then high-shear mixing at  $\phi \leq 0.45$ , or manual stirring at  $\phi > 0.45$ , until a smooth appearance was achieved. Using a glycerol-water mixture slows evaporation and sedimentation, both of which can prevent accurate rheology. The glycerol content was adjusted to access the maximum range of stresses in each sample ( $0.1 \text{ Pa} \lesssim \sigma \lesssim 400 \text{ Pa}$ ). We checked that varying the amount of glycerol did not strongly change the rheology or qualitatively influence our conclusions.

We used three surfactants: polyacrylic acid (PAA); an alkyl-naphthalene sulphonate condensate (ANS), Morwet D-425; and a polycarboxylate ether (PCE), Agrilan 755. PAA adsorbs to calcite forming a monolayer (Eriksson et al., 2007). Our PAA was a linear 5100 Da sodium salt (Sigma Aldrich) with a 3 nm gyration radius (Reith et al., 2002). Commercial ANS is a highly-polydisperse mixture of oligomers with branched and cross-linked chains (Piotte et al., 1995) often used as “superplasticisers” in self-compacting concrete (Mehta, 1999). The PCE is a comb co-polymer of polyethylene glycol grafted to a methacrylate-methylmethacrylate backbone. Similar surfactants are known to stabilise calcite suspensions (Bossis et al., 2017).

Surfactants were dissolved into the glycerol-water mixture before powder incorporation at concentrations reported as weight percentages relative to the solid content (w/w%). The main concentrations used were 0.05 w/w% (PAA), 0.5 w/w% (ANS) and 1.0 w/w% (PCE), which were chosen as the concentration needed in each case before no further change was found in the rheology of a  $\phi = 0.44$  sample if more is added (see Appendix).

Steady-state flow curves were measured using parallel plates (radius  $R = 20 \text{ mm}$  and gap height  $H = 1 \text{ mm}$ ) that were sandblasted or serrated to reduce slip. For suspensions



without surfactant, controlled shear rate measurements were taken (TA Instruments ARES-G2, roughened plates). We report the rim shear rate,  $\dot{\gamma} = \Omega R/H$  from the applied angular velocity,  $\Omega$ ; the stress,  $\sigma = (\mathcal{T}/2\pi R^3)(3 + d \ln \mathcal{T}/d \ln \Omega)$  from the measured torque,  $\mathcal{T}$ ; and hence the relative viscosity,  $\eta_r = \sigma/(\dot{\gamma}\eta_s)$ .

Samples were pre-sheared at high stress to remove the loading history, before applying a single upsweep at 5 points per decade from the minimum shear rate,  $\dot{\gamma}_{\min} = 0.1 \text{ s}^{-1}$ , to sample fracture at  $\sigma_{\max} \approx 400 \text{ Pa}$ . At each point the longer of  $\gamma = 10$  or  $t = 10 \text{ s}$  was accumulated with an average of the steady state taken. The minimum shear rate is set by the longest experiment limited by sedimentation below  $\sigma_{\min} = \Delta\rho g d \approx 0.1 \text{ Pa}$ . When strong shear thinning is observed we identify an experimental yield stress,  $\sigma_y = \sigma(\dot{\gamma}_{\min})$ .

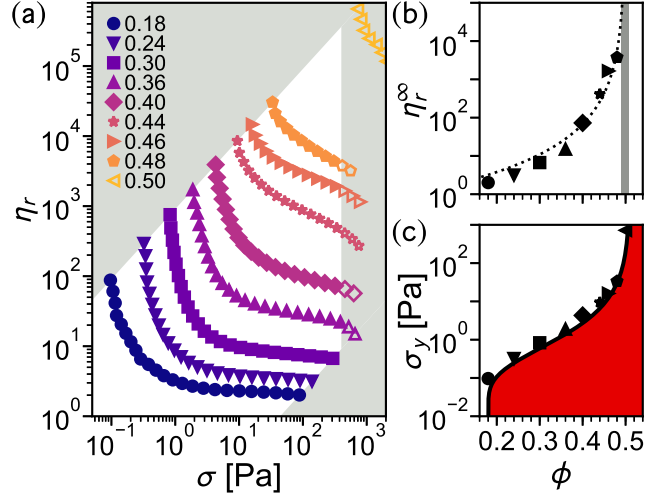
Measurements with surfactants used imposed stress (serated plates, TA Instruments DHR-2 for ANS and PCE, AR-2000 for PAA). After a 1 Pa pre-shear, 10 points per decade were measured between  $\sigma_{\min}$  and fracture or inertial sample ejection, always ensuring reversibility below fracture. At each point, measurement followed a 5 s equilibration, but the total time per point was adjusted between samples to maximise the averaging time while still avoiding sedimentation. For PAA and PCE the step time was 10 s for  $\phi \leq 0.4$ , 20 s for  $0.45 \leq \phi \leq 0.49$  and 30 s for  $\phi \geq 0.51$ ; for ANS a single step time of 15 s was used. For systems where the shear rate may decrease with stress (discontinuous shear thickening), we report the apparent stress,  $\sigma_{\text{app}} = 2\mathcal{T}/\pi R^3$ .

## Results

Suspensions of bare calcite particles in an 85 wt.% glycerol-water mixture ( $\eta_s = 110 \text{ mPa s}$ ) show strong shear thinning at all measured  $\phi$ , Fig. 3(a), consistent with the presence of a yield stress below which flow ceases. At  $\phi < 0.40$ , the viscosity decreases towards a high-shear plateau,  $\eta_r^\infty$ . At higher  $\phi$  any plateau value is obscured by sample fracture (open symbols). At  $\phi = 0.50$  all flow may be due to fracture. In all cases, we take  $\eta_r^\infty$  to be the viscosity at the highest stress before fracture.

The absence of shear thickening suggests that the system is always frictional. This is confirmed by fitting Eq. 1 to  $\eta_r^\infty(\phi)$ , giving divergence at  $\phi_\mu = 0.50(1)$  [with  $\ell = 2.6(3)$ ], Fig. 3(b). With  $\sigma_y \approx \sigma_{\min}$  at  $\phi = 0.18$ , it was not possible to measure a yield stress for lower  $\phi$  without sedimentation; so, we take (as an upper bound)  $\phi_{\text{alp}} = 0.18$ . Using an adhesive strength of  $\sigma_a \approx 0.6 \text{ Pa}$  (and  $\kappa = 0.6$ ) in the constraint model of Eq. 5 with  $f = 1$  and Eq. 4 then predicts a  $\phi$ -dependence of  $\sigma_y$  that accounts well for our observations, Fig. 3(c).

Physically, Fig. 3(c) tells us that at low  $\phi$  the suspension flows at all applied stresses. When  $\phi$  reaches 0.18, it becomes possible for adhesion to stabilise the frictional contact network enough for the system to jam. However, this



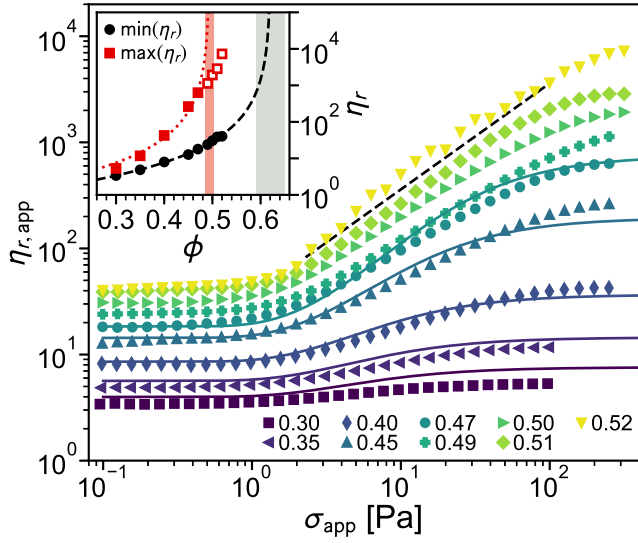
**Fig. 3** Steady-state rheology of bare calcite suspensions. (a) Relative viscosity vs stress,  $\eta_r(\sigma)$ , under imposed shear rate. Symbols, data at volume fraction,  $\phi$  (legend). Shading (grey) outside measurable limits. (b) High-shear relative viscosity,  $\eta_r^\infty(\phi)$ . Symbols,  $\eta_r$  before fracture; dotted line,  $\eta_r^\infty = (1 - \phi/\phi_\mu)^{-\ell}$ ,  $\phi_\mu = 0.50(1)$  [shading (grey)] and  $\ell = 2.6(3)$  (c) Yield stress,  $\sigma_y$ , vs volume fraction. Symbols, yield stress from minimum shear rate,  $\sigma_y = \sigma(\dot{\gamma}_{\min} = 0.1 \text{ s}^{-1})$ . Solid line,  $\sigma_y$  with  $\theta \rightarrow \infty$ , from Eqs. 4 and 5 ( $f = 1$  and  $\phi_{\text{alp}} = 0.18$ ), taking  $\sigma_a = 0.6 \text{ Pa}$  and  $\kappa = 0.6$ . Shaded (red), jammed; and unshaded, flowing

adhesion-stabilised frictional network breaks above a finite applied stress,  $\sigma_y$ , and the system flows. As  $\phi$  increases, the frictional network acquires additional stability, and more adhesive bonds need to be broken to fluidise the suspension:  $\sigma_y$  increases. Eventually, upon reaching  $\phi_\mu$ , no adhesive stabilisation is needed - the frictional network is stable in its own right: the system is jammed at all stresses and  $\sigma_y \rightarrow \infty$ .

Thus, bare calcite particles in a glycerol-water mixture form a frictional suspension: little or no stress is needed to push the particles into frictional contact because  $\sigma^* \rightarrow 0$ . This onset stress can be made finite by introducing a repulsive barrier between particles, which then must be overcome to press particles into mechanical contact. This can be done, e.g., via electrostatic surface effects by modifying the dissolved ions (Al Mahrouqi et al., 2017). We will tune the repulsive barrier sterically using surfactants.

When PAA is added (70 wt.% glycerol-water mixture,  $\eta_s = 22.5 \text{ mPa s}$ ), the suspension no longer shows any evidence of a finite yield stress, Fig. 4 (symbols). Instead, the viscosity rises from a low-shear to a high-shear plateau at increasing stress, with the magnitude of the effect increasing with volume fraction. This is classical shear thickening.

In detail, at  $\phi \leq 0.47$ , suspensions continuously thicken to a high-shear plateau, but for  $\phi > 0.47$  a plateau is not reached before fracture. At the highest measured  $\phi = 0.52$ , we see discontinuous shear thickening, indicated by  $d \ln \eta_r / d \ln \sigma > 1$  [dashed line]. Fitting  $\eta_r^\infty(\phi)$  to Eq. 1, Fig. 4 [inset (red)], gives the frictional jamming point  $\phi_J = \phi_\mu = 0.49(1)$  [with



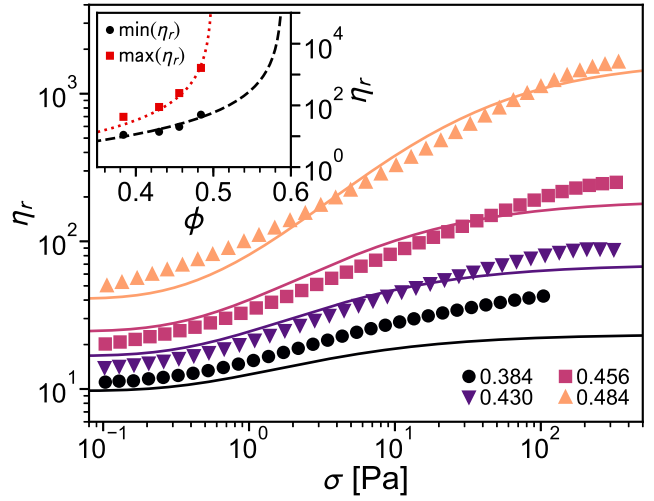
**Fig. 4** Flow curves of polyacrylic acid (PAA) stabilised calcite suspensions. Symbols: apparent relative viscosity vs stress,  $\eta_{r,app}(\sigma_{app})$ , at volume fraction,  $\phi$  (legend). Dashed (black) line, DST (slope = 1). Solid lines, WC model ( $\theta \rightarrow 0$ ) fit to  $\phi \leq 0.47$ , onset stress  $\sigma^* = 3.0(2)$  Pa ( $\beta = 1.02$ ). Inset: plateau viscosity with volume fraction. Squares (red): high-shear viscosity from  $\max(\eta_r)$ ; circles (black), low-shear viscosity from  $\min(\eta_r)$ . Dotted (red) line, fit of Eq. 1, to find  $\phi_J = 0.49(1)$  [shading (red)] and  $\ell = 2.2(2)$ . For  $\min(\eta_r)$  a pre-factor,  $A = 0.8(1)$ , is included in Eq. 1 [dashed (black) line], to give  $\phi_J = 0.62(3)$  [shading (grey)]

$\ell = 2.2(2)$ ], the same as the high stress  $\phi_J$  for bare calcite suspensions to within error.

The absence of any observable shear thinning implies that  $\sigma_a \rightarrow 0$ . The observation of shear thickening means that, instead,  $\sigma^*$  is now finite: a repulsive interaction must be overcome to press particles into mechanical contact, so that  $\theta \rightarrow 0$ . With this stabilising repulsive interaction, the viscosity should diverge only at random close packing at  $\sigma \rightarrow 0$ . Fitting  $\eta_r^0(\phi)$  to Eq. 1, Fig. 4 [inset (black)], we find that, indeed,  $\phi_J = 0.62(3)$  [with  $\ell = 2.2(4)$ ], consistent with the value of  $\phi_J = 0.60$  determined separately using a powder compaction test (DS/EN 1097-4:2008). Using our two fitted values of  $\phi_{rcp}$ ,  $\phi_\mu$  and  $\ell = 2.2$ , from the high-shear viscosity divergence, we fit Eq. 2 to our data to find  $\sigma^* = 3.0(2)$  Pa (and  $\beta = 1.02$ ).

For ANS (in 85 wt.% glycerol-water mixture,  $\eta_s = 110$  mPa s), a similar transition from a yield stress fluid to a shear-thickening suspension is seen, Fig. 5 (symbols). Repeating the same analysis procedure, we find  $\phi_{rcp} = 0.59(1)$  and  $\phi_\mu = 0.499(3)$ , Fig. 5 (inset), consistent with the PAA data. Again, the flow curves suggest that  $\sigma_a \rightarrow 0$ , and fitting Eq. 2 to the data now gives  $\sigma^* = 1.0(1)$  Pa, so that, again  $\theta \rightarrow 0$ .

The effect of the third surfactant, PCE (in 50 wt.% glycerol-water mixture,  $\eta_s = 6$  mPa s), is similar at moderate to high stresses,  $\sigma \gtrsim 1$  Pa, Fig. 6 (symbols). We see continuous shear thickening to a plateau at  $\phi \leq 0.47$  and to fracture at higher concentrations. On the other hand, we now see shear thinning



**Fig. 5** Flow curves for alkyl-naphthalene sulphonate condensate (ANS) stabilised calcite suspensions. Symbols: relative viscosity vs stress,  $\eta_r(\sigma)$ , at volume fraction,  $\phi$  (legend); lines, WC model ( $\theta \rightarrow 0$ ) fit,  $\sigma^* = 1.0(1)$  Pa ( $\beta = 0.67$ ). Inset: limiting  $\phi_J$  used in WC model. Symbols: squares (red),  $\max(\eta_r)$ , high-shear viscosity; circles (black),  $\min(\eta_r)$ , low-shear viscosity. Lines: dotted (red), fit of Eq. 1 to  $\max(\eta_r)$  with  $\ell = 2.2$  fixed from Fig. 4 to find  $\phi_J = 0.499(3)$ ; dashed (black), fit to  $\min(\eta_r)$  to find  $\phi_J = 0.59(1)$

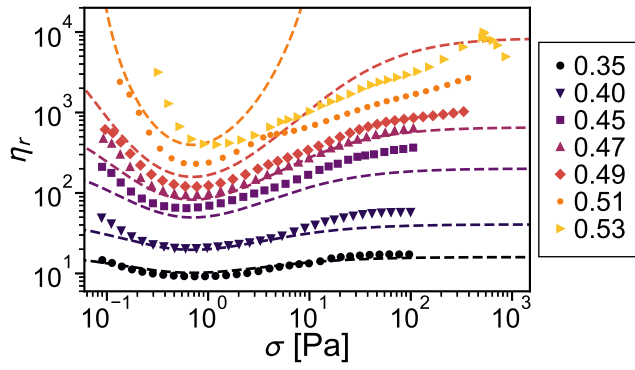
at  $\sigma \lesssim 1$  Pa, with the appearance of a small yield stress at the highest solid volume fractions,  $\sigma_y \approx 0.2$  Pa at  $\phi = 0.51$ . This value is, however, negligible compared to that of the bare calcite suspension at this volume fraction ( $\gtrsim 400$  Pa).

Fitting  $\eta_r^\infty(\phi)$  to Eq. 1 gives same frictional jamming point,  $\phi_\mu = 0.49(1)$  ( $\ell = 2.3$ ), as before. Fixing  $\phi_{rcp} = 0.62$ ,  $\phi_{alp} = 0.18$ ,  $\beta = 0.67$  and  $\kappa = 0.6$  from previous fittings, we find that the constraint model can give a reasonable account of the observed trends using  $\sigma_a = 0.3$  Pa and  $\sigma^* = 3$  Pa, Fig. 6 (dashed lines), so that  $\theta \approx 0.1$ .

## Discussion and conclusions

In the constraint rheology framework, the effect of adding surfactants is a matter of tuning the relative magnitudes of the two relevant characteristic stress scales,  $\sigma^*$ , beyond which sliding constraints form rapidly, and  $\sigma_a$ , beyond which rolling constraints break rapidly. The values of ( $\sigma^*$ ,  $\sigma_a$ ) we have deduced, Table 2, should be taken as no more than order of magnitude estimates: varying the procedure used in inferring them from data would have given different results; but this does not alter the qualitative picture.

Dispersing bare nB calcite particles in a glycerol-water mixture gives suspensions in which a finite yield stress emerges at  $\phi \gtrsim 0.18$  before jamming at all stresses at  $\phi \gtrsim 0.5$ , the frictional jamming point,  $\phi_\mu$ . The yield stress is due to adhesion of strength  $\sigma_a \sim 0.6$  Pa stabilising inter-particle frictional contacts, which form at infinitesimal applied stress, i.e., the onset stress  $\sigma^*$  is vanishingly small. Adding any of



**Fig. 6** Flow curves of polycarboxylate ether (PCE) stabilised ground calcite in a 50 wt.% glycerol-water mixture. (a) Relative viscosity vs stress,  $\eta_r(\sigma)$ . Symbols, data at volume fraction,  $\phi$  (legend); dashed lines, Eqs. 1-5 with representative parameters, see text

the three surfactants confers a finite  $\sigma^*$  of order  $\sim 10^0$  Pa. The difference between the surfactants is that while adding PAA and ANS reduces the adhesive strength to being immeasurably small,  $\sigma_a \rightarrow 0$ , adding PCE only decreases this stress scale by a factor of 2. Notably, this modest reduction in the adhesive strength still results in a large drop in the yield stress at, e.g.,  $\phi = 0.40$  from 4 Pa to  $\ll 0.1$  Pa, a factor of 40 (at least). With a large onset stress,  $\theta \ll 1$ , there is now no frictional contact network for adhesion to stabilise: frictional contacts are the primary determinants of the ability of the suspension to withstand finite applied stress.

Our PCE data, Fig. 6, resemble those for hydrophobised glass spheres in water (Brown et al., 2010). Brown et al. suggest that adding surfactant ‘eliminates . . . clustering with its associated yield stress and reveals a region of underlying shear thickening.’ Instead, our data indicate the converse: that surfactants reduce  $\sigma_y$  in adhesive nB suspensions primarily by imparting a finite onset stress below which there can be no frictional network for inter-particle adhesion to stabilise.

Strikingly, the concentration at which the high-shear viscosity diverges for all three systems with surfactants occurs at  $\phi \approx 0.50$  within experimental uncertainties, which is the frictional jamming point of the bare calcite suspension. At high applied stress, particles in the systems with surfactant additives interact as if they were bare. We interpret this as follows. Adding the amount of surfactant we used in each case provides approximately monolayer covering to the bare calcite particles providing a degree of steric stabilisation. Now, a finite stress,  $\sigma^*$ , is needed to push them into frictional contact. Thus,  $\sigma^*$  is a measure of the stress needed to displace adsorbed surfactants from the calcite surface. Once the surfactant is displaced, the frictional interaction is again that between bare particles, accounting for the same  $\phi_\mu$  in all four suspensions.

In the case of PAA adsorbing on calcite, we can show quantitatively that this is a reasonable suggestion. The adsorption energy of 2000 Da PAA (we used 5100 Da) on calcite at room temperature is  $E = 15 \text{ kJ mol}^{-1} \approx 6k_B T$  per polymer

Surfactant	$\sigma^*$ [Pa]	$\sigma_a$ [Pa]	$\theta = \frac{\sigma_a}{\sigma^*}$	$\sigma_y$ [Pa] at $\phi = 0.40$	$\phi_\mu$
None	$\rightarrow 0$	0.6	$\rightarrow \infty$	4	0.50(1)
PAA	3	$\rightarrow 0$	$\rightarrow 0$	$\rightarrow 0$	0.49(1)
ANS	1	$\rightarrow 0$	$\rightarrow 0$	$\rightarrow 0$	0.50
PCE	3	0.3	0.1	$\ll 0.1$	0.49

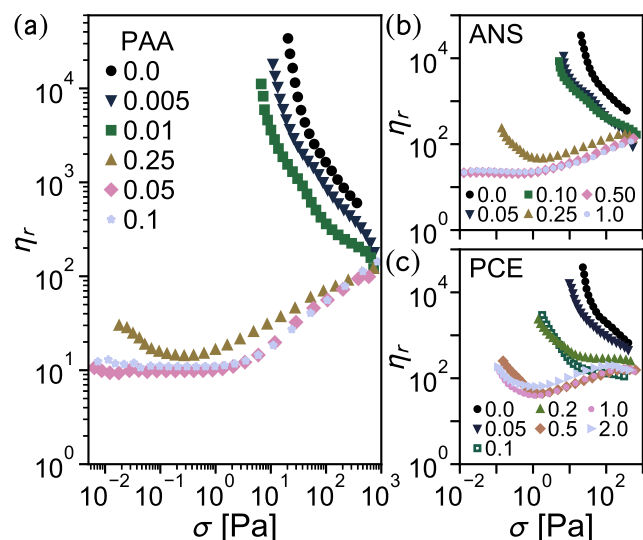
**Table 2** Estimates of characteristic stresses in calcite suspensions without and with surfactants. For each system: frictional onset stress,  $\sigma^*$ ; adhesive strength,  $\sigma_a$ ; stress scale ratio,  $\theta$ ; yield stress,  $\sigma_y$ , at  $\phi = 0.40$ ; and the fitted frictional jamming point,  $\phi_\mu$

coil (Sparks et al., 2015). This allows us to estimate a local critical stress scale for desorption  $\sigma_0^* = E/R_g^3 \sim 10^6$  Pa, which can be converted into the area of contact when friction is turned on,  $r_0^2$ , by equating the bulk and local forces,  $\sigma_0^* r_0^2 \sim \sigma^* d^2$ , for particles of linear size  $d$ . This gives  $r_0 \sim 7 \text{ nm}$ , which is plausibly the length scale of surface roughness; so the picture is that  $\sigma^*$  is the external stress needed to drive adsorbed PAA from asperities, exposing these to interact frictionally. This highlights the role of surfactant adsorption at the local level, as raised by Mantellato and Flatt (2020) for partial coverage of superplasticiser in cementitious suspensions.

These findings lead to a new design principle for using surfactants to ‘tune’ the rheology of nB adhesive suspensions. Given two surfactants that are equally effective as steric stabilisers, i.e., in lowering  $\sigma_a$ , the one that is more strongly adsorbed, i.e., with the higher adsorption energy  $E$ , should give a higher  $\sigma^*$  and therefore be more effective in lowering  $\sigma_y$ . Indeed, in the limit of a high enough  $\sigma^*$  relative to  $\sigma_a$ , adhesive bonds are all broken before any frictional contact network can be formed. The latter can therefore never be stabilised by adhesion, and a yield stress cannot emerge below  $\phi_\mu$ . Thus,  $\sigma_y$  is reduced from some finite value to zero for all  $\phi < \phi_\mu$ , as is observed when we add PAA or ANS, Table 2. Such use of surfactants to confer a finite onset stress for nB adhesive suspensions to give essentially an infinite-fold reduction in the yield stress is perhaps the main, and certainly the most surprising, conclusion of this work, generalising a similar but less clear-cut finding in the use of surfactants to tune the rheology of molten chocolate (Blanco et al., 2019).

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**Fig. 7** Effect of surfactant concentration. (a) Variation of polyacrylic acid (PAA) sodium salt. Symbols, relative viscosity as a function of stress,  $\eta_r(\sigma)$ , at a volume fraction,  $\phi = 0.44$ , in a 50 wt.% glycerol-water mixture with PAA concentration weight percentage relative to calcite (w/w%), legend. (b) Alkyl-naphthalene sulphonate condensate sodium salt (ANS) variation. (c) Polycarboxylate ether (PCE) variation

**Data availability** The datasets generated during and/or analysed during the current study are available in the Edinburgh DataShare repository, <https://doi.org/10.7488/ds/2875>.

**Conflict of interest** The authors declare that they have no competing interests.

## Appendix: Choosing surfactant concentrations

Three surfactants, PAA, ANS and PCE, were used in this work to modify the interaction between calcite particles. We determined the concentration used for detailed investigation in each case by measuring the flow curve for a  $\phi = 0.44$  suspension in a 50 wt.% glycerol-water mixture at increasing surfactant concentration until we reached the point where a further increase does not bring about further changes in the rheological behaviour. Measurements were made under imposed shear rate (TA Instruments ARES-G2, sandblasted plates) with a sweep at 6 points per decade from  $\dot{\gamma}_{\min} = 0.1 \text{ s}^{-1}$  using a fixed step time of 20 s equilibration and 10 s of measurement. Note that as the PCE was supplied in a liquid form, we take the active component to be 50 wt.% based on the product specification. The addition of surfactants at the concentrations used was found not to affect the glycerol-water mixture viscosities.

The data collected in this process are shown in Fig. 7 for the three surfactants. For all cases we see a saturation in the effect of the surfactant, with no further change in the rheology measured after 0.05 w/w% for PAA, 0.5 w/w% for ANS and 1 w/w% for PCE and the concentration at saturation is used for the experiments reported in the main text. [Note that a single anomalous flow curve was seen for 0.1 w/w% PCE, Fig. 7(c); this is possibly due to sample under-filling.]

The amount of surfactant needed to achieve saturation effect can be understood quantitatively in the case of the PAA we used, which has a gyration radius of  $R_g \approx 3 \text{ nm}$ . It is easy to estimate that at 0.05 w/w%, PAA coils of area  $\sim R_g^2$  can cover  $\approx 0.5 \text{ m}^2/\text{g}$  of calcite

surfaces. Separately, modelling our calcite particles as spheres with diameter  $d = 4 \mu\text{m}$ , we estimate that the suspension has a specific surface area of  $\approx 0.5 \text{ m}^2/\text{g}$ , although this is only an estimate due to asphericity and polydispersity. The saturation concentration therefore credibly represents complete monolayer coverage. We may surmise that the same may be true for the other two surfactants. This finding lends credence to our suggestion that the finite onset stress conferred by surfactants at the saturation concentration scales with the local stress needed to dislodge adsorbed surfactant molecules.

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